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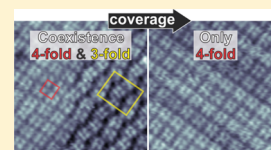
Coverage-Dependent Structural Transformation of Cyano-Functionalized Porphyrin Networks on Au(111) via Addition of Cobalt Atoms

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Supporting Information

ABSTRACT: The self-assembly process of a cobalt-porphyrin derivative (Co-TCNPP) containing cyanophenyl substituents at all four meso positions on Au(111) was studied by means of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) under ultrahigh vacuum conditions. Deposition of Co-TCNPP onto Au(111) gave rise to the formation of a close-packed H-bonded network, which was independent of coverage as revealed by STM and LEED. However, a coverage-dependent structural transformation took place upon the deposition of Co atoms. At monolayer coverage, a reticulated long-range ordered network exhibiting a distinct fourfold Co coordination was observed. By reduction of the molecular coverage, a second metal–organic coordination network (MOCN) was formed in coexistence with the fourfold Co-coordinated network, that is, a chevron structure stabilized by a simultaneous expression of H-bonding and threefold Co coordination. We attribute the coverage-dependent structural transformation to the in-plane compression pressure exerted by the molecules deposited on the surface. Our study shows that a subtle interplay between the chemical nature of the building blocks (molecules and metallic atoms) and molecular coverage can steer the formation of structurally different porphyrin-based MOCNs.



INTRODUCTION

The possibility of fabricating metal–organic frameworks (MOFs) in three dimensions (3D) possessing remarkable functional properties—also in view of applications—by applying concepts of supramolecular chemistry has eventually granted protocols for the construction of low-dimensional nanoarchitectures on surfaces.^{1,2} That is, two-dimensional (2D) metal–organic coordination networks (MOCNs) on surfaces have been realized by means of self-assembly and possess promising applications in gas storage, catalysis, and energy conversion chemistry.^{3–6} The formation of structurally different MOCNs can be achieved by carefully selecting the organic building blocks and metallic species to which they coordinate to.^{7–9} Especially, porphyrins have been shown to be stable and versatile building blocks for the construction of MOCNs displaying different coordination geometries, as their backbone can be tailored with specific functional endgroups.^{10–13} Despite the extensive literature available for MOCNs on surfaces, there are only a few studies focused on the influence of molecular coverage on the self-assembly of such structures upon varying the molecule–metal ratio.^{14,15} This is in contrast to the abundant reports discussing coverage-dependent phenomena for low-dimensional purely organic arrangements on surfaces.^{16–21} Similar to these findings, the in-plane compression pressure built by the molecules on the surface, which increases with molecular coverage, is expected to result in changes of the MOCN with respect to its structure, molecular conformation, and/or coordination environment.

Herein, we present a study of the influence of molecular coverage on the self-assembly process of cobalt(II) 5,10,15,20-(tetra-4-cyanophenyl)porphyrin (Co-TCNPP) before and

after coordination with Co atoms on Au(111) by means of scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Co-TCNPP, as shown in Figure 1, is a tetrapyrrolic macrocycle functionalized at all four meso

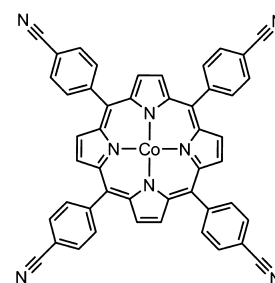


Figure 1. Chemical structure of cobalt(II) 5,10,15,20-(tetra-4-cyanophenyl)porphyrin (Co-TCNPP).

positions by cyanophenyl substituents, with each cyano endgroup pointing outward and its core contains a Co atom. The STM and LEED measurements showed that the deposition of Co-TCNPP on Au(111) gave rise to a long-range ordered close-packed H-bonded network that is invariant to the changes of in-plane compression pressure exerted by molecular coverage. After the deposition of Co atoms with a fixed molecule to metal ratio (~1:1 with a slight excess of metal), a coverage-dependent structural transformation took

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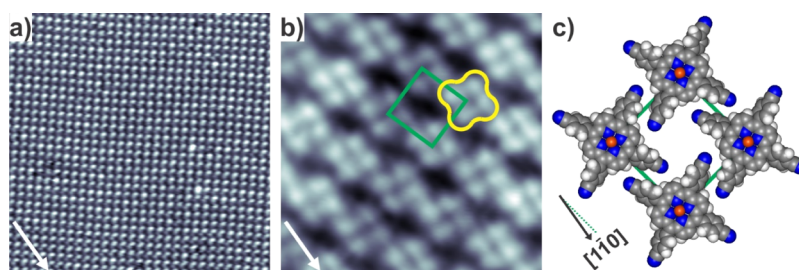


Figure 2. Self-assembly of the close-packed H-bonded network of Co-TCNPP on Au(111). (a) Overview STM image showing the long-range order of the 2D network stabilized by H-bonding ($50 \times 50 \text{ nm}^2$, $U_{\text{bias}} = 1.6 \text{ V}$, $I_{\text{set}} = 20 \text{ pA}$). (b) High-resolution STM image in which the phenyl moieties of the macrocycle are discernible ($7.5 \times 7.5 \text{ nm}^2$, $U_{\text{bias}} = 2 \text{ V}$, $I_{\text{set}} = 15 \text{ pA}$). The yellow outline and green square highlight one porphyrin and the unit cell, respectively. (c) Tentative structural model of the H-bonded close-packed network. Cobalt, nitrogen, carbon, and hydrogen atoms are shown in orange, blue, gray, and white, respectively. The unit cell of the network is shown in green. In (c), the dotted green line is parallel to a unit cell direction and the black arrow indicates a principal direction of the Au substrate. In (a,b), the white arrow at the bottom denotes a principal crystallographic direction of the Au substrate.

place that modified the coordination geometry of the Co atoms located at the coordination nodes. At monolayer coverage, the formation of a distinct long-range ordered fourfold MOCN was observed in which the Co atoms adopted a rare square planar coordination geometry. Upon decreasing the molecular coverage of Co-TCNPP and keeping the stoichiometric ratio between molecules and metal-atoms constant, a second MOCN was formed in coexistence with the fourfold MOCN, that is, a chevron structure stabilized by a simultaneous expression of H-bonding and threefold metal coordination. In such structures, the Co atoms are arranged in a distorted tetrahedral coordination geometry. Based on the premise of the in-plane compression pressure built from the molecules on the surface, the subtle balance between the cyanophenyl-substituents and molecular coverage makes the self-assembly of this porphyrin-based MOCN an interesting alternative to investigate the adsorption behavior of structurally different MOCNs on metal surfaces. To the best of our knowledge, we present the first coverage-dependent long-range ordered porphyrin-based MOCN on a bare metal surface, while keeping the molecule-metal atom ratio constant.

Experimental Methods. All experiments were carried out in an ultrahigh vacuum (UHV) system (with a base pressure in the low 10^{-10} mbar regime) equipped with different chambers for sample preparation and characterization. The Au(111) single crystal was cleaned by repeated cycles of Ar^+ sputtering and annealing at 720 K. The porphyrin derivatives (PorphyrChem) were thermally sublimed at 820 K onto the Au(111) surface held at room temperature (RT) by means of a Knudsen cell evaporator (OmniVac). Cobalt atoms were deposited onto the organic layer from a cobalt rod using an e-beam evaporator (Oxford Applied Research). During metal deposition, the substrate was held at 410 K. For comparison, the deposition of Co atoms was also performed at RT (see Figure S4 in the Supporting Information). The molecule-metal ratio was kept fixed ($\sim 1:1$ with a slight excess of metal). A quartz crystal microbalance was used to monitor the molecule and metal atom deposition rates. STM measurements were conducted with a commercial low-temperature STM (Scienta Omicron GmbH) operated at RT with a mechanically cut Pt/Ir wire as a tip in the constant current mode. All bias voltages are given with respect to a grounded tip. The STM images were processed with WSxM software.²² In addition, the LEED patterns were acquired using a microchannel plate LEED (Scienta Omicron GmbH) and simulated with LEEDPat4.2 software.²³

RESULTS

Co-TCNPP on Au(111). The deposition of a monolayer of Co-TCNPP on Au(111) held at RT gave rise to a close-packed network displaying the long-range order as evidenced in the overview STM image of Figure 2a. The molecules arranged in a square-like fashion. The high-resolution STM image in Figure 2b unveils in detail the molecular appearance of Co-TCNPP and its orientation with respect to the neighboring porphyrin units. Individual porphyrins (highlighted in yellow) can be distinguished by four bright lobes attributed to the peripheral phenyl moieties. Such an appearance is typical for phenyl-substituted porphyrins on metallic substrates.^{24–27} It should be noted that the cyano endgroups did not contribute to the STM contrast.^{28,29} The metallic center in the porphyrin core is not visible in the STM image under the given tunneling conditions.^{24–26,30,31} Furthermore, the varying brightness between consecutive molecules is induced by the underlying herringbone reconstruction of the Au substrate, which was well preserved underneath the molecular layer (see Figure S1a in the Supporting Information). Based on our STM and LEED measurements, we propose a square unit cell (depicted in green in Figure 2b) with dimensions $a = b = 1.68 \pm 0.05 \text{ nm}$ and an internal angle of $\alpha = 90^\circ \pm 2^\circ$. The molecular density for this arrangement is equal to 0.35 Co-TCNPP molecules per nm^2 . Moreover, our STM and LEED measurements (see Figure S2 in the Supporting Information) suggest that the unit cell (cf. dotted green line in Figure 2c) is rotated 7.5° with respect to the principal Au directions. The incommensurability of the close-packed network with the underlying Au substrate was confirmed by the absence of the integer matrix elements in the superstructure matrix of the simulated LEED pattern (see Figure S2 in the Supporting Information). This adsorption behavior might be induced when the molecule–molecule interactions outweigh over site-specific interactions with the substrate.^{32,33}

In addition to the molecular appearance (Figure 2b), the lateral molecular orientation with respect to the neighboring porphyrin units can also be discerned. The corresponding tentative structural model is depicted in Figure 2c. The molecules are rotated 19° with respect to the unit cell axis (shown in green) and align their cyanophenyl substituents toward the pyrrole moieties of neighboring Co-TCNPP units. Such a configuration allows the formation of a H-bond between the electronegative N atom of the terminal cyano endgroup and a hydrogen bonded to a sp^2 -hybridized carbon

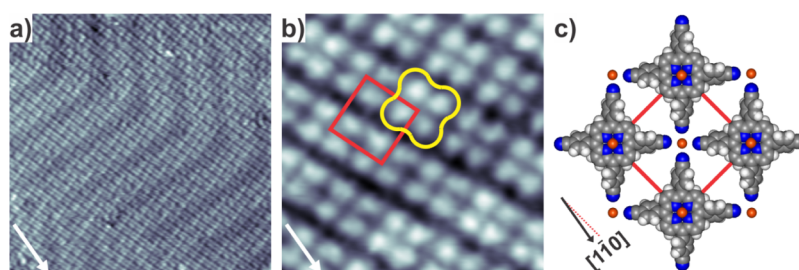


Figure 3. Self-assembly of the fourfold Co-coordinated network at monolayer coverage of Co-TCNPP with Co atoms on Au(111). (a) Overview STM image showing the long-range order of the 2D network stabilized by metal-coordination ($50 \times 50 \text{ nm}^2$, $U_{\text{bias}} = 2 \text{ V}$, $I_{\text{set}} = 15 \text{ pA}$). The Au herringbone reconstruction is visible through the molecular ad-layer. (b) High-resolution STM image in which the phenyl moieties of the macrocycle are discernible ($7.5 \times 7.5 \text{ nm}^2$, $U_{\text{bias}} = 2 \text{ V}$, $I_{\text{set}} = 15 \text{ pA}$). The yellow outline and red square highlight one porphyrin and the unit cell, respectively. (c) Tentative structural model of the fourfold Co-coordinated network. Cobalt, nitrogen, carbon, and hydrogen atoms are shown in orange, blue, gray, and white, respectively. The unit cell of the network is shown in red. In (c), the dotted red line is parallel to a unit cell direction and the black arrow indicates a principal direction of the Au substrate. In (a,b), the white arrow at the bottom denotes a principal crystallographic direction of the Au substrate.

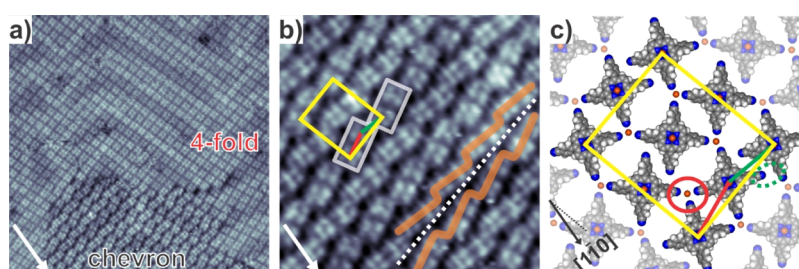


Figure 4. Self-assembly of submonolayer coverage of Co-TCNPP on Au(111) after deposition of Co atoms. (a) Overview STM image ($50 \times 50 \text{ nm}^2$, $U_{\text{bias}} = 2 \text{ V}$, $I_{\text{set}} = 15 \text{ pA}$). The molecules and Co atoms assembled into two MOCNs: a fourfold Co-coordinated network (text in red) and a close-packed chevron structure (text in black). (b) Zoom-in STM image of the close-packed chevron structure ($17 \times 17 \text{ nm}^2$, $U_{\text{bias}} = 2 \text{ V}$, $I_{\text{set}} = 15 \text{ pA}$). The yellow rectangle highlights the unit cell, while the red and green lines resemble the lengths highlighted in the structural model in (c). The grey rectangles enclose two pairs of Co-TCNPP molecules within a single row of molecules. The white dotted line guides the eye between two mirrored rows of molecules (denoted by the orange zig zag lines). (c) Tentative structural model of the chevron structure. Cobalt, nitrogen, carbon, and hydrogen atoms are shown in orange, blue, gray, and white, respectively. The unit cell of the network is shown in yellow. The red and green lines are equal in length to the unit cell axes of the fourfold Co-coordinated network and to the close-packed H-bonded network, respectively. Analogously, the solid red and dotted green ovals highlight the Co-coordination and H-bonding motifs, respectively. In (c) the dotted black line is parallel to a unit cell direction and the black arrow indicates a principal direction of the Au substrate. In (a,b), the white arrow at the bottom denotes a principal crystallographic direction of the Au substrate.

atom from a pyrrole moiety of an adjacent molecule. The projected H–N distance is approximately 3.2 \AA and falls within typical H-bond distances ($1.5\text{--}3.5 \text{ \AA}$).^{4,14} The Co-TCNPP molecules also assembled into the aforementioned close-packed H-bonded network at sub-monolayer coverage (see Figure S1b in the Supporting Information). Such an arrangement is similar to the previously reported 2D assembly of a free-base tetracyanophenyl porphyrin (2H-TCNPP) on Ag(111).²⁶

Co-TCNPP on Au(111) after Co Coordination. The deposition of the required amount of Co-TCNPP followed by the addition of Co atoms (while keeping the substrate at 410 K) for a full monolayer of fourfold MOCN (maintaining a fixed $\sim 1:1$ molecule-metal ratio with a slight excess of metal) gave rise to a well-ordered 2D network as shown in the overview STM image of Figure 3a. The molecules were arranged into a network displaying a grid-like appearance. The herringbone reconstruction of the Au(111) surface translates through the molecular layer, similar to the observations described for the close-packed H-bonded network (see Figures 2b and S1a). The long-range order of the network with domains that extend over $>100 \text{ nm}$ is supported by LEED measurements (see Figure S3 in the Supporting Information). Nonetheless, domain boundaries stabilized by H-bonding

between islands of the 2D network were infrequently found (see Figure S4a in the Supporting Information).

The high-resolution STM image in Figure 3b reveals features of the network structure. Within the envelope of a single Co-TCNPP unit (highlighted in yellow) the phenyl moieties are again imaged as bright lobes,^{24–27} as previously discussed for the H-bonded network. The metallic center in the porphyrin core is not imaged at a positive bias as shown in Figure 3b. Once again, the varying brightness between consecutive molecules is given by the underlying herringbone reconstruction of the Au substrate. From our STM and LEED measurements, we determined a square unit cell (depicted in red) with dimensions $a = b = 1.79 \pm 0.02 \text{ nm}$ and an internal angle of $\alpha = 90^\circ \pm 3^\circ$. The molecular density now amounts to $0.31 \text{ Co-TCNPP molecules per nm}^2$. Our STM and LEED measurements (see Figure S3 in the Supporting Information) suggest that the unit cell (cf. dotted red line in Figure 3c) is rotated 7.5° with respect to the principal Au directions. In contrast to the lateral molecular orientation with respect to neighboring porphyrins in the H-bonded network (Figure 2b), the molecules no longer align their cyanophenyl substituents towards the phenyl moieties of a neighboring molecule but rather are arranged in a head-to-head configuration pointing to a common fourfold node. By taking into consideration the

repulsive nature between nucleophilic species, the formation of a fourfold node between the terminal N atoms without a coordinating metal atom can be ruled out. Hence, such a configuration gives evidence of a metal–ligand bonding. Indeed, the lone pair electrons provided by the N atoms of the cyano endgroups possess high binding affinity towards transition metals.^{34–36} Therefore, as illustrated in the tentative structural model (Figure 3c), we propose that this network is a MOCN stabilized by a fourfold coordination node with one Co atom (orange sphere) coordinating to a total of four molecules, resulting in a 1:1 stoichiometric ratio between Co-TCNPP and Co atoms as evidenced by STM. The electro-negative N atom of the terminal cyano endgroup interacts via metal–ligand bonding with the Co atom, with a projected Co–N distance of approximately 2.5 Å. The common invisibility of 3d transition metals within 2D MOCNs on metallic surfaces prevails for the Co atoms located at the coordinating nodes (Figure 3a,b).^{8,9,34}

To assess the adsorption behavior of Co-TCNPP in terms of molecular coverage, we deposited a sub-monolayer coverage of molecules on Au(111), followed by Co deposition with the sample kept at 410 K. The stoichiometric ratio between the molecules and metal atoms was fixed ($\sim 1:1$ with a slight excess of metal) throughout all our experiments to only focus on the influence of molecular coverage in the self-assembly of Co-TCNPP. As evidenced by the overview STM image in Figure 4a, the formation of a second different network took place, that is, a chevron structure (highlighted with black text) coexisted with the fourfold Co-coordinated network (highlighted with red text) in the lower and upper half, respectively. The higher molecular density of the fourfold Co-coordinated network with respect to the chevron structure is clearly noticeable. The herringbone reconstruction of the Au(111) substrate was still intact as seen in Figure 4a.

A closer inspection of the chevron structure is shown in Figure 4b. The common bright lobe contrast given by the phenyl moieties prevails for each Co-TCNPP molecule and the varying brightness between consecutive porphyrins is given by the herringbone reconstruction of the Au substrate. From our STM measurements, we determined a unit cell (depicted in yellow) with dimensions $a = 3.54 \pm 0.03$ nm and $b = 4.26 \pm 0.04$ nm and an internal angle of $\alpha = 90^\circ \pm 3^\circ$. The molecular density of this structure is equal to 0.27 Co-TCNPP molecules per nm². The Co-TCNPP molecules arranged in pairs following a tail-to-tail configuration as outlined by the grey rectangles (two Co-TCNPP molecules per rectangle). The tiling of successive pairs formed rows of molecules as depicted by the orange zigzag lines. A peculiarity of the chevron structure is its chirality (the white dotted line guides the eye between two mirrored rows). Accordingly, as depicted in the tentative structural model (Figure 4c), we propose that the network is stabilized by a simultaneous expression of H-bonding and metal–ligand interactions:^{14,15} (i) a threefold metal-coordination (solid red oval) between the cyano endgroups from three different Co-TCNPP molecules and one Co atom and (ii) H-bonding (dashed green oval) between consecutive porphyrin pairs following the geometry of a T-type interaction.³⁷ Interestingly, the 1:1 stoichiometric ratio between the molecules and Co atoms prevailed for the chevron structure. The solid red and green lines in Figure 4b,c are in agreement with the unit cell vector values reported for the fourfold Co-coordinated and the close-packed H-bonded networks, respectively. Furthermore, the threefold metal-

coordination node is distorted, that is, the angle between the Co-TCNPP molecules is not symmetrical and deviates from the previously reported values of 120° for Co-coordinated MOCNs.^{6,7} The chevron structure coexisted as a minority phase with the fourfold Co-coordinated network in a ca. 30:70 coverage ratio for samples prepared at sub-monolayer coverage at a range of around 0.75 ML. However, the chevron structure did not form as one exclusive phase and postannealing treatments did not promote the formation of one exclusive phase. These results confirm that the chevron and fourfold Co-coordinated assemblies are coverage-dependent and the latter is formed as one exclusive phase at monolayer coverage.

DISCUSSION

Over the last decades, numerous studies on the formation of MOFs in 3D have been realized and explained with concepts of supramolecular chemistry.^{1,2} In cases where Co atoms are used as metallic centers within the MOF, they are known to prefer coordinating with organic ligands in an octahedral or tetrahedral coordination geometry in 3D crystalline structures.^{38–41} However, the coordination geometry of metal atoms is likely to be modified on a surface, because the underlying substrate takes away one dimension. Consequently, the number of coordination sites available to interact with the organic ligands is reduced. Additionally, the substrate can either take the role of a ligand or not. In particular, on noble metal surfaces, threefold coordination motifs are known to prevail for Co atoms with cyano-functionalized molecules.^{6,7,34,38} In our study, the chevron structure observed at sub-monolayer coverage is stabilized by a distorted threefold coordination motif present in the 2D plane parallel to the Au(111) substrate. We reason that such a configuration could only occur if hybridization between the Co atoms (located at the coordination nodes) and the Au substrate takes place. Therefore, the Co atoms at the nodes might have adopted a distorted tetrahedral coordination geometry with the three cyano endgroups located in the plane of MOCN and the Au substrate acting as the fourth ligand. Our reasoning is based on the findings for linear dicyanonitrile–polyphenyl molecules and Co atoms adsorbed on Ag(111) for which hybridization between the Co and Ag atoms was concluded, which prompted the formation of a metal–organic nanomesh stabilized by threefold Co-coordination nodes.⁷

As described above, the chevron structure always co-existed as a minority phase with the fourfold Co-coordinated network at sub-monolayer coverage. In a previous study, a similar grid-like MOCN formed on a noninteracting substrate (hBN) and allowed the formation of fourfold Co coordination motifs.²⁷ In contrast, we observed the formation of such coordination motifs on a bare metal surface, namely, Au(111). In comparison to the chevron structure and in analogy to the fourfold coordinated MOCN on hBN,²⁷ we conclude that the Co atoms located at the nodes of the fourfold Co-coordinated network are no longer hybridized with the Au substrate and interact with four cyano endgroups via a square planar coordination geometry. Obviously, the introduction of the Au(111) substrate modified the expected coordination geometry encountered for Co atoms in 3D crystalline structures. Similarly, we deposited a nickel analogue of Co-TCNPP on Au(111), and the results are in line with the fourfold Co-coordinated network discussed here (see Figures S5–S7 in the Supporting Information).

Furthermore, the coverage-dependent behavior of Co-TCNPP upon coordination became evident at monolayer coverage, where the fourfold Co-coordinated network formed as one exclusive phase. The influence of molecular coverage on the self-assembly of organic networks^{16–21} and MOCNs^{14,15} has been previously reported to lead to the transformation of one type of structure into a second, mostly more densely packed structure. Such a transformation is driven by the so-called intrinsic in-plane compression pressure, which is built up from the molecules adsorbed on the surface and increases with molecular coverage. The literature describing the coverage-dependent adsorption behavior of porphyrin-based networks has been rarely reported.^{20,21} In our study, the higher molecular density of the fourfold Co-coordinated network compared to the chevron structure (0.31 and 0.27 Co-TCNPP molecules per nm², respectively) increases the in-plane compression pressure in the 2D plane of the MOCN. This promotes a dense molecular packing between the Co-TCNPP molecules and Co atoms following a square planar coordination geometry, which has been so far only reported for Co-coordinated MOCNs on noninteracting surfaces like hBN^{27,42} and 3D crystalline structures.^{43–45} To the best of our knowledge, we present the first coverage-dependent long-range ordered MOCN stabilized by a fourfold Co-coordination motif observed for a tetracyanophenylporphyrin derivative on a bare metal surface.

Along with the in-plane compression pressure, the different energetic contributions must be considered to better understand the coverage-dependent behavior of Co-TCNPP upon coordination with Co atoms. To compare both MOCNs in terms of Gibbs free energy, we will consider the following factors: (i) the intermolecular interactions in the MOCN, (ii) the molecule substrate interactions, and (iii) the surface area covered by the molecules (molecular density). The chevron structure is stabilized by a combination of H-bonding and metal–ligand interactions, whereas only metal–ligand interactions are present in the fourfold Co-coordinated network. In general, metal–ligand interactions are stronger than H-bonds and should bring the system to a lower energetic state. With respect to the molecule substrate interactions, we assume that they are similar for both the threefold and the fourfold Co-coordinated structures despite the identified different rotational arrangements of the molecules with respect to the principal Au directions. We arrived at that conclusion because both structures are not commensurate to the substrate, and thus the molecules do not favor a specific adsorption position. Furthermore, the overall energy of the system can also be lowered by increasing the number of molecules per surface area. Such is the case of the fourfold Co-coordinated network that minimizes the surface area occupied per molecule.

However, the threefold coordination motif of the chevron structure should be preferred according to the coordination geometries reported for 3D structures. Thus, to assemble the molecules in the fourfold coordination motif, the fourfold MOCN pays an energetic penalty through its higher molecular density observed with respect to the chevron structure. In general, we can conclude that the overall energy is considered to be small (based on the above arguments) due to the observed co-existence of both MOCNs and that is the reason why the fourfold Co-coordinated network can be promoted as one exclusive phase at monolayer coverage.

CONCLUSIONS

In summary, we investigated the influence of molecular coverage on the self-assembly of Co-TCNPP before and after coordination with Co atoms on Au(111) by STM and LEED under UHV conditions. The deposition of Co-TCNPP on Au(111) gave rise to a close-packed H-bonded network that showed to be invariant to the changes in molecular coverage. However, upon metal-coordination with Co atoms a coverage-dependent structural transformation took place, which also modified the coordination geometry of the Co atoms located at the coordination nodes. At monolayer coverage, the in-plane compression pressure exerted by the molecules on the surface steered the formation of a fourfold Co-coordinated network that exhibited a distinct square planar coordination geometry for the Co atoms located at the coordination nodes. By reducing the molecular coverage, a second MOCN was formed in co-existence with the fourfold MOCN, that is, a chevron structure stabilized by a simultaneous expression of H-bonding and threefold Co coordination. In this MOCN, the Co atoms adopted a distorted tetrahedral coordination geometry, which is the coordination geometry expected in 3D structures. Furthermore, the fourfold MOCN paid an energetic penalty to have all Co-TCNPP molecules in the square planar coordination geometry by, among others, reducing the surface area occupied per molecule. In addition, as observed at monolayer coverage, a MOCN stabilized by only metal–ligand interactions such as the fourfold Co-coordinated network will bring the system to a lower energetic state compared to MOCNs that contain weaker bonding motifs like the H-bonding found in the chevron structure. Therefore, a subtle interplay between the chemical nature of the building blocks and molecular coverage can steer the formation of structurally different MOCNs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b05055.

Additional STM and LEED data of Co-TCNPP before and after coordination with Co-atoms on Au(111) and STM and LEED data of Ni-TCNPP after coordination with Co-atoms on Au(111) (PDF)

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Notes

The authors declare no competing financial interest.

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